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Division of Environmental Chemistry

– Chemistry for Functionalized Surfaces –

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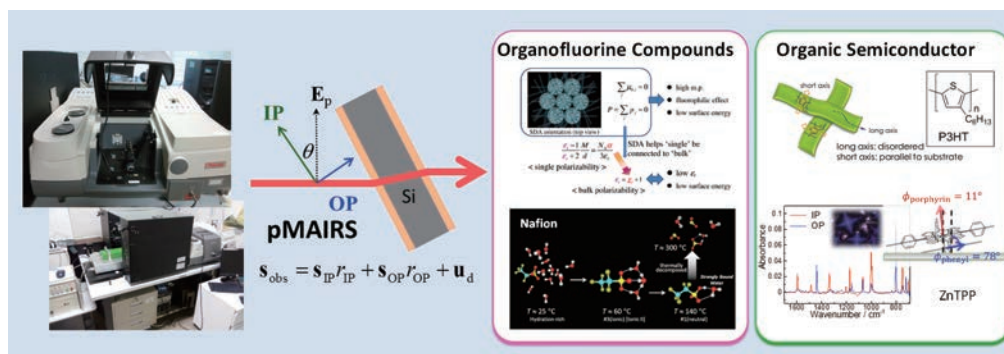
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Scope of Research

To understand the chemical structure and properties of a molecular aggregated system, the keywords of molecular interactions and orientation are focused on, and the molecular aggregates are investigated by using originally developed spectroscopic techniques. The current major topics are: (1) perfluoroalkyl-specific properties in a condensed system; (2) controlling factors of molecular packing and orientation in a thin film of an organic semiconductor compound; (3) development of new molecular orientation analytical technique “MAIRS2.”

KEYWORDS

Infrared and Raman Spectroscopy
Surface and Interface Chemistry
Perfluoroalkyl Compounds
Organic Semiconductor
pMAIRS and MAIRS2



Selected Publications

Shioya, N.; Hada, M.; Shimoaka, T.; Murdey, R.; Eda, K.; Hasegawa, T., Impact of Kinetically Restricted Structure on Thermal Conversion of Zinc Tetraphenylporphyrin Thin Films to the Triclinic and Monoclinic Phases, *J. Phys. Chem. C*, **122**, 4540-4545 (2018).

Tomita, K.; Shioya, N.; Kise, R.; Shimoaka, T.; Yoshida, H.; Koganezawa, T.; Eda, K.; Hasegawa, T., Structure Control of a Zinc Tetraphenylporphyrin Thin Film by Vapor Annealing Using Fluorine Containing Solvent, *Thin Solid Films*, **665**, 85-90 (2018).

Shimoaka, T.; Ukai, H.; Kurishima, K.; Takei, K.; Yamada, N.; Hasegawa, T., Molecular Aggregation of Perfluoroalkyl Groups Can Win the Hydrogen Bonding between Amides, *J. Phys. Chem. C*, **122**, 22018-22023 (2018).

Isozaki, K.; Shimoaka, T.; Oshiro, S.; Yamaguchi, A.; Pincella, F.; Ueno, R.; Hasegawa, T.; Watanabe, T.; Takaya, H.; Nakamura, M., Robust Surface Plasmon Resonance Chips for Repetitive and Accurate Analysis of Lignin–Peptide Interactions, *ACS Omega*, **3**, 7483-7493 (2018).

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Tokunaga, A.; Mutoh, K.; Hasegawa, T.; Abe, J., Reversible Valence Photoisomerization between Closed-Shell Quinoidal and Open-Shell Biradical Form, *J. Phys. Chem. Lett.*, **9**, 1833-1837 (2018).

Impact of Kinetically Restricted Structure on Thermal Conversion of Zinc Tetraphenylporphyrin Thin Films to the Triclinic and Monoclinic Phases

The powerful combination of p-polarized multiple-angle incidence resolution spectroscopy (pMAIRS) and grazing incidence X-ray diffraction (GIXD) is applied to the structural characterization of zinc tetraphenylporphyrin (ZnTPP) in vapor-deposited films as a function of the deposition rate. The deposition rate is revealed to have an impact on the initial film structure and its conversion by thermal annealing. The pMAIRS spectra reveal that a fast deposition rate yields a kinetically restricted amorphous film of ZnTPP having a “face-on orientation,” which is readily discriminated from another “randomly oriented” amorphous film generated at a slow deposition rate. In addition, the GIXD patterns reveal that the film grown at a slow deposition rate involves a minor component of triclinic crystallites. The different initial film structure significantly influences the thermal conversion of ZnTPP films. The randomly oriented amorphous aggregates with the triclinic crystallite seeds are converted to the thermodynamically stable phase (monoclinic) via the metastable triclinic phase. The kinetically restricted structure, on the other hand, is followed by a simple thermal conversion: the molecules are directly converted to the monoclinic one rather than the triclinic one.

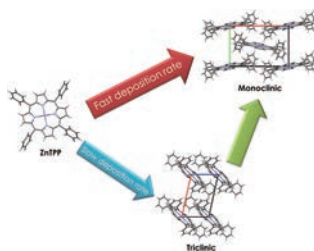


Figure 1. Schematic summary of the different two thermal conversions of ZnTPP thin films grown at fast and slow deposition rates.

Structure Control of a Zinc Tetraphenylporphyrin Thin Film by Vapor Annealing Using Fluorine Containing Solvent

The solvent vapor annealing (SVA) technique is one of the useful post processing techniques of a thin film, which is an alternative technique of the thermal annealing one. SVA has a great advantage that the molecular rearrangement in the film is made moderately by employing an appropriate solvent without the sample heating. The moderate processing is expected to yield a benefit that the molecular coalescence would be suppressed, which would readily keep the continuous surface topography of the film during the annealing, and another benefit that a metastable structure would be obtained. To make the best use of the SVA-specific characteristics, in the present study, a material having a metastable structure is chosen. The sample is

ZnTPP that yields a metastable triclinic crystal structure, which can easily be converted to a monoclinic crystal structure by thermal annealing. A triclinic-structure film of ZnTPP by the combination of a wet process and the thermal annealing has thus never been reported. By choosing a fluorine-containing solvent, which has a low affinity to ZnTPP, a triclinic-structure film has first been obtained by a wet process while the surface continuity is protected.

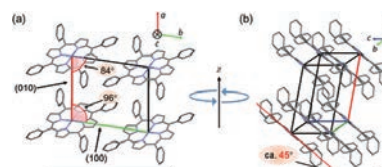


Figure 2. The schematics of molecular orientation of the triclinic crystallite from the two viewpoints.

Molecular Aggregation of Perfluoroalkyl Groups Can Win the Hydrogen Bonding between Amides

Hydrogen bonding is, in general, recognized to have a much stronger molecular interactive force than the dipole–dipole interaction that is one of the van der Waals forces. The molecular interaction between perfluoroalkyl (Rf) chains is driven by a two-dimensional dipole–dipole interaction network because of a large dipole moment along the C–F bond and a helical conformation about the Rf chain axis, which generates the Rf-specific tight and closed molecular packing. The polarization of a molecular aggregate on a macroscopic scale comprehensively explains the Rf compound-specific properties represented by the high melting point. This cooperative interaction in the two-dimensional network gives us an impression that the dipole–dipole interaction can win the H-bonding in a molecular aggregate. In the present study, amphiphilic compounds having an Rf group and an amide group are prepared, and the molecular aggregation factor is investigated by means of surface chemistry and vibrational spectroscopic techniques. In fact, we show that the dipole–dipole interaction becomes the dominant factor of the molecular aggregation of the amide-containing compound.

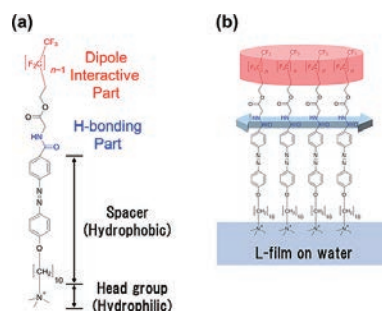


Figure 3. (a) Chemical structure of the amphiphilic compounds having an Rf group and an amide group, and (b) schematic image of a molecular aggregation of molecules on water.